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PREFACE

The undersigned constitute the planning committee for this project. Professor E. J. Smoke is project leader. The experimental work has been carried out by Mr. Peter Fleischner and Mr. Chester Ringel.

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DEVELOPMENT OF REFRACTORY CERAMICS THAT CAN BE  
PROCESSED AT TEMPERATURES CONSIDERABLY LOWER THAN  
THEIR MAXIMUM USE TEMPERATURE

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Since this is a progress report, the information  
contained herein is tentative and subject to changes,  
corrections and modifications.

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## ABSTRACTS

### Part I. Presintering Studies

The presintering study was initiated to determine the densification mechanisms of a high alumina body utilizing the presintering process, an analysis of phase reactions with regard to equilibrium conditions are shown. Conclusions from the overall study are presented.

### Part II. Sintering Studies

A study of the densification of pure alumina (C), pure alumina with 0.25% MgO (R) and pure alumina containing 2.0% MgO (CR) was carried out in a vacuum. Procedures are outlined for the study of the densification of these three compositions in dry hydrogen and dry helium. In addition three other compositions will be used with the three aforementioned compositions to determine the limits of solid solution of MgO in  $Al_2O_3$ .

### Part III. Devitrification Studies

Cordierite compositions were fritted with the frit utilized as the basic raw material. Density and moisture absorption results and devitrification and maturing temperatures are presented.

## I. PRESINTERING STUDY

### A. Introduction

This study was initiated in order to better understand the mechanisms occurring in a presintering operation of high alumina compositions. Once these mechanisms are determined and controlled, it should be possible to obtain an optimum body under a given set of conditions. This will play a vital role in the overall, objective of this effort, the lowering of the firing temperature of ceramics for radome application, yet retaining all the desirable engineering properties.

The previous reports dealt with the preparation and initial investigations into the aspects of density and phase investigations of a study in which the object was to determine the dependence in the initial firing of: raw materials, firing temperature, phase formation, density, and sintering mechanisms upon the resultant body achieved in the final firing operation. From this study, the parameters involved with regard to their role in the formation of the beneficial phases in the final firing operation. In this report the aspects of: equilibrium, phase formation, densification mechanisms, impure raw materials, and liquid phase formation are discussed. The conclusions obtained from the overall study are presented.

### B. Equilibrium

From the phase diagram, it can be seen that any mixture of  $Al_2O_3$ ,  $MgO$ ,  $SiO_2$ , may result in some liquid formation above

1347°C, the lowest invariant point of the system. This liquid formation is local and transitory for all mixtures outside the subsystem silica-clinsenstatite-cordierite, and will immediately begin to disappear by reaction with the crystalline phases present to yield the equilibrium phases. This non-equilibrium melting is non-permanent and little more than incipient. This melting has the effect of greatly facilitating chemical reaction of the ingredients. This non-equilibrium melting, while important has no bearing on the vitrification of a ceramic body. The equilibrium melting which takes place at the invariant temperature for the compatibility triangle enclosing a particular composition is the primary factor dealing with vitrification.

The compositions investigated all lie within the compatibility triangle alumina-mullite-spinel. The invariant temperature for this triangle is 1575°C. As the temperature is increased, the oxides will react to form all possible phases, if only on a very local basis. There would be non-equilibrium melting for each particular subsystem as the temperature was increased above the invariant temperature of the subsystems. Above 1475°C, the invariant temperature for the cordierite-spinel-mullite triangle, only alumina, mullite and spinel will co-exist in equilibrium for the compositions investigated. At 1575°C, the invariant temperature of the subsystem, equilibrium melting begins. If equilibrium conditions were attained throughout, vitrification would not occur below 1575°C.



Series 72, 73, and 74 were fired for a prolonged period of time to determine the phases which would exist with some degree of stability at the various temperatures studied. These conditions, although not equilibrium conditions, serve to show in what direction the reactions are proceeding. The object is to study the phase relationship between a composition prepared from a raw material of arrested reactions and the same composition under equilibrium conditions.

## 2. Procedure

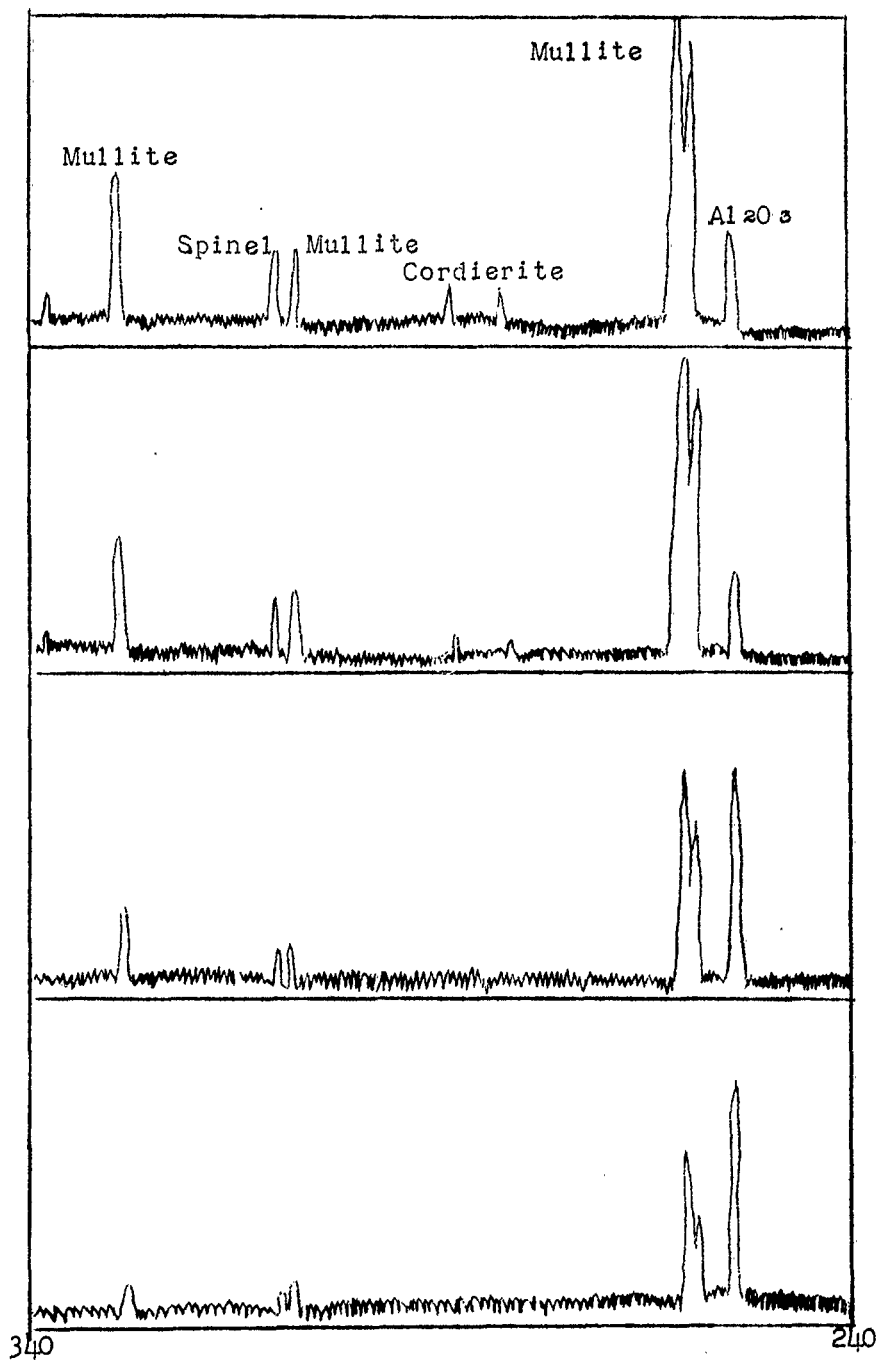
Samples of series 72, 73, and 74 were prepared utilizing the presintering process. The prereacted material of these compositions was used in the fabrication of discs to be studied. The discs were placed in a platinum crucible and fired in a platinum wound resistance furnace. The temperature was recorded by means of two thermo-couples, one connected to a potentiometer and the other attached to a temperature controlling recording device. The sample was heated to the required temperature, held at that temperature for 17 hours, then quenched in water. After crushing to pass -200 mesh, the sample was analyzed by X-ray analysis.

## 3. Series 72

The X-ray diffraction patterns of the Series 72, 71.8%  $Al_2O_3$  - 21.15%  $SiO_2$  - 7.05%  $MgO$ , present a detailed picture of the phase changes occurring with an increase in final firing

X-RAY DIFFRACTION PATTERN FINAL FIRE SERIES 72

Figure 1



temperature. The temperature range studied encompasses the entire critical firing range from the underfiring through overfiring of this type composition.

The critical factor in the densification appears to be the decrease in the height of the mullite peaks with an increase in temperature. Since no other crystalline phase containing silica is evidenced, it is assumed that the dissociation of the mullite results in a glassy phase and free alumina. The decrease in the height of the spinel peaks with an increasing temperature indicates that some magnesia is going into the glass. The alumina peaks therefore are increasing in size as a result of the dissociation of the mullite and spinel.

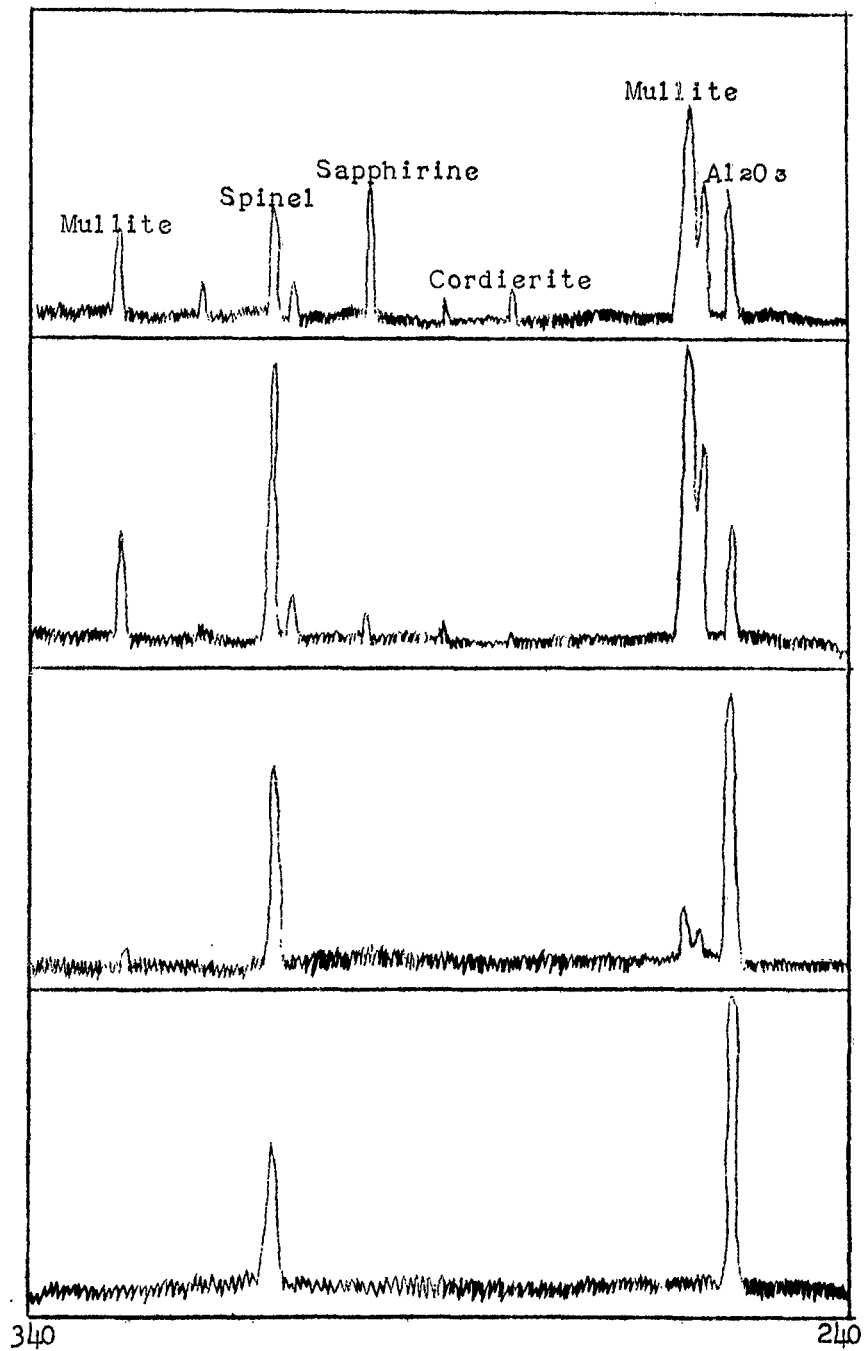
The phase diagram indicates that this composition, at equilibrium, should contain only two phases, mullite and spinel. The temperatures studied are below the invariant temperature of this subsystem, thus no liquid phase should be present. This study indicated that this composition does not conform with the equilibrium phase diagram with regard to the temperatures involved.

#### 4. Series 73

The X-ray diffraction patterns, shown on pages of the Series 73, 71.8%  $Al_2O_3$ -14.1%  $SiO_2$ -14.1%  $MgO$ , present a detailed picture of the phase changes occurring with an increase in the final firing temperature. The temperature range studied encompasses the firing range from under firing through overfiring of this type composition.

X-RAY DIFFRACTION PATTERN FINAL FIRE SERIES 72

Figure 2



Once again, as in Series 72, the critical factor in the densification appears to be the decrease in the height of the mullite peaks with an increase in temperature. This series differs from Series 72 only in the relative degree of dissociation of the mullite peaks with an increase in temperature. In this series, the mullite peaks are very rapidly decreasing with an increase in temperature above 2650°F, and are not perceptible at 2800°F. Once again, the spinel peaks are decreasing with an increase in temperature.

Since no other crystalline phases containing silica are present, it is assumed that the dissociation of the mullite results in a glassy phase and free alumina. The decrease in the height of the spinel peaks indicates that some magnesia is going into the glass. Thus, this composition densifies with the aid of a liquid phase.

The phase diagram indicated that this composition, at equilibrium, should contain only two phases, mullite and spinel. The temperatures studied are below the invariant temperature of the subsystem, thus, no equilibrium liquid phase should be present. The study of this composition indicates that there is no conformity with the phase diagram with regard to temperature.

#### 5. Series 74

The X-ray diffraction pattern of the Series 74, 71.8%  $Al_2O_3$  - 7.05%  $SiO_2$  - 21.15%  $MgO$ , present a detailed picture of the phase changes occurring with an increase in final firing temperature. The temperature range studied encompasses the firing range from underfiring through overfiring of this type composition.

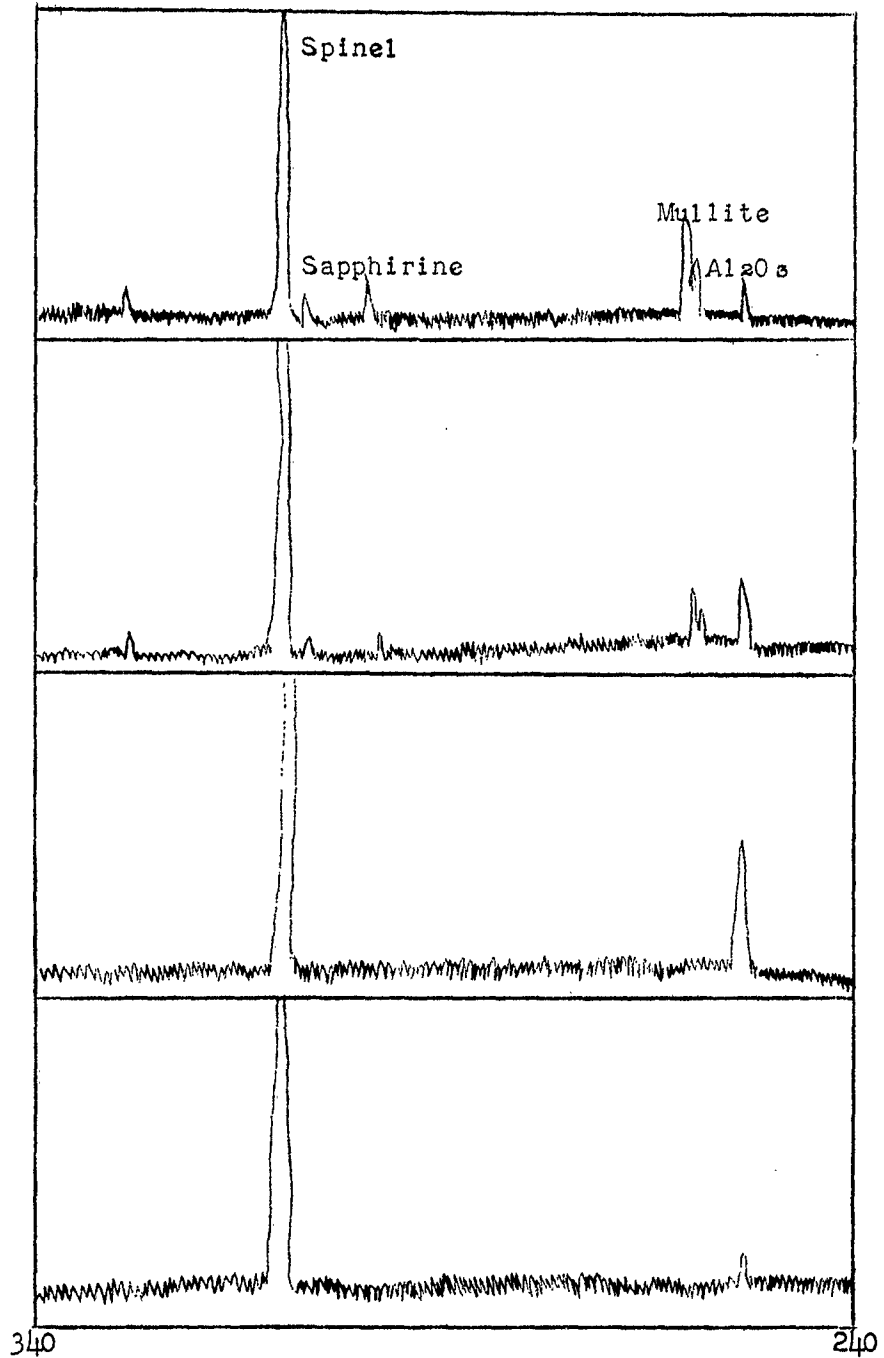
As in Series 72 and 73, the critical factor in the densification appears to be the decrease in the height of the mullite peaks with an increase in temperature. This series differs from Series 72 and 73 in two respects. The dissociation of the mullite peaks with an increase in temperature is occurring more rapidly, such that no peaks are perceptible at 2700°F. The spinel peaks are increasing with an increasing temperature while the alumina peaks are decreasing. This is the opposite effect to that occurring in Series 72 and 73.

Since no other crystalline phases containing silica are present, it is assumed that the dissociation of the mullite results in a glassy phase and free alumina. Thus, this composition densifies with the aid of a liquid phase.

The phase diagram indicated that this composition, at equilibrium, should contain only two phases, mullite and spinel. The temperatures studied are below the invariant temperature of the subsystem alumina-spinel-mullite, thus no equilibrium liquid phase should be present. This study indicates that this

X-RAY DIFFRACTION PATTERN-FINAL FIRE SERIES 72

Figure 3



composition does not conform to the equilibrium phase diagram with regard to temperature. However, the increasing content of liquid with an increasing temperature, the rapid dissociation of the mullite, and the increasing content of the primary field phase are indications of equilibrium conditions.

### C. Dissociation of Mullite

#### 1. Introduction

From the correlation between the densification curves and the X-ray results, it is evident that the dissociation of the mullite introduces a liquid phase which is primarily responsible for the densification mechanisms. The mullite dissociates well below the invariant temperature for this subsystem under equilibrium conditions.

Compositions were prepared utilizing extremely pure raw materials and prepared by utilizing spinel and mullite as raw materials in order to determine if impurities or non-equilibrium phases are primarily responsible for the low temperature dissociation of the mullite.

#### 2. High Purity Compositions

A composition of 71.8%  $Al_2O_3$  - 21.15%  $MgO$  - 7.05%  $SiO_2$  was prepared by incorporating extremely pure raw materials. (Linde "A"  $Al_2O_3$  - 99.99%  $Al_2O_3$ ;  $MgNO_3$  - 99.8% purity; and Cab-O-Sil 99.99%  $SiO_2$ ). The object was to determine the role of the impurities in the non-equilibrium dissociation of mullite about 2700°F.



X-ray results show that mullite was present in sizeable quantity with a final firing of 2600°F. Increasing the final firing to 2700°F, it was seen that the mullite peaks were barely perceptible. At 2800°F, the mullite peaks were completely gone. These results were similar to those obtained for Series 73.

This would give good indication that the presence of impurities in the raw materials are not primarily responsible for the low temperature dissociation of the mullite peaks.

### 3. Equilibrium Compositions

A composition of 71.8%  $Al_2O_3$  - 14.10%  $SiO_2$  - 14.10%  $MgO$  was prepared utilizing spinel and mullite as the raw materials. The object was to determine the role of non-equilibrium phases with regard to the non-equilibrium dissociation of the mullite about 2700°F.

The spinel and mullite were formed by presintering raw materials of these compositions. The mullite compositions were fired twice at 2800°F to allow the maximum mullite formation. The spinel composition reached completion of reaction with a single firing of 2800°F. Proper proportions were barely perceptible, and with a final firing of 2800°F, no mullite peaks were observed.

This would give good indication that the presence of non-equilibrium phases in the raw materials for the final firing are not primarily responsible for the dissociation of the mullite at the low temperature observed.

D. Discussion on Equilibrium

Ternary compositions studied showed that in the initial firing the phase reactions were proceeding in the direction of equilibrium conditions as set forth by the equilibrium phase diagram. However, the time and temperature utilized were insufficient to allow the reactions to reach completion.

In the final firing, the phase reactions continued to proceed along these equilibrium lines only to firing temperatures below 2650°F above this temperature, the mullite begins to dissociate into a liquid and free alumina. The relative decrease in the height of the mullite peaks and the temperature at which they disappear is strongly dependent upon the amount of magnesia present. With an increase in firing temperature, the spinel content decreases and the alumina content increases for compositions containing 2:1 and 1:1 silica to magnesia ratios. For compositions containing 1:2 silica to magnesia ratios, the alumina decreases and the spinel content increases.

These reactions occurring in the final firing operation conform to the equilibrium phase diagram with respect to their order of disappearance into a liquid, but do not conform to the temperatures at which these reactions are to occur. Considering that firing, grinding, and then firing again should lead to completeness of reaction, there is some doubt arising regarding the invariant temperature of the subsystem. It appears that the liquid formed is of an equilibrium type, since an increase in temperature will result in the formation of greater liquid content.

However, other factors must be considered. The first factor is the sluggishness of reactions between the oxides used in this study. The second factor is that the raw material used in the second firing are compounds formed by arresting the reactions before they are allowed to go to completion. If we consider the raw materials in the second firing to be only spinel, mullite, and alumina, then the phase diagram must be given closer scrutiny as to its accuracy. But in all instances, these compounds, as well as the non-equilibrium phases arrested in the initial firing are the raw materials. Thus, the final firing is not a three phase system, but can have as many components as were formed in the initial firing. In all cases, ternary phases were formed which would make the system a four component one at the very least. These many component systems give rise to complex phase reactions and liquid formation not described by the phase diagram as they proceed toward an equilibrium assemblage.

Taking all these factors into consideration, it is felt at the present time that non-equilibrium reactions are primarily responsible for the liquid phase formation which aids densification in the final firing operation. The results attained in this study are of such a nature that they appear to resemble equilibrium conditions. However, there is no conformity with the equilibrium phase diagram.

E. Conclusions From Study

1. Compositional Conclusions

- a. Compositions containing only alumina and silica do not attain maturity below 2900°F. Compositions investigated containing magnesia matured in the range 2700° - 2800°F.
- b. Increasing the silica content resulted in an increased degree of overfiring and slumping.
- c. Increased alumina content results in increased density and strength.
- d. Holding the alumina constant, and increasing the magnesia content while decreasing the silica content resulted in increased density and extended firing range.
- e. Upon variation of the particle size of the initial raw material, it was found that only the size of the silica was critical. A fine particle size silica composition possessed a substantially higher density than a similar composition containing a coarser variety, while the size of the alumina and magnesia showed no marked increase in density with an increasing particle size.
- f. In the range, 71.8 - 95.0% alumina content, compositions containing similar ratios of magnesia to silica ratios have identical phase formation occurring and similar density curves for the temperature range studied.

- g. The thermal expansion was shown to increase as the magnesia replaced the silica in a constant alumina content composition.

## 2. Temperature Conclusions

- a. Presintering in the range 2600-2800°F gives optimum densities at lowest temperatures.
- b. Final firing at 2700°F is necessary to mature all compositions with the exception of those along the alumina-silica binary. An increase of firing temperature to 2800°F overfires the low alumina compositions, and an increase to 2900°F overfires all the ternary compositions.

## 3. Grinding Operation

- a. Grinding results in an intimate mixing of the pre-sintered raw material.
- b. Grinding reduces the particle size, and gives a particle size distribution, such as to aid in densifying the composition in the final firing.
- c. Grinding removes the large void content of the extruded rods by grinding out the voids.

## 4. Presintering Fire

- a. The presintering fire is primarily a phase formation process.

- b. There is very little densification occurring owing to the large volume of voids introduced from binder, water, and gases. The temperatures utilized were too low for solid state diffusional mechanisms to play a large role.
- c. The fired extruded rods were quite porous, which is beneficial for facilitating the grinding operation.
- d. Final densities of ternary compositions are equivalent when compositions are presintered to 2600°, 2700°, or 2800°F. If a low presintering, 2000°F, is utilized, the final firing temperature must be increased to achieve equivalent densities of higher presintered compositions.

## 5. Phase Formation

### a. Presintering Fire

- i) A presintering fire of 2000°F results in a raw material in which there is only slight phase reaction among the compound oxides.
- ii) A presintering fire of 2600°F produces phase reactions which result in the formation of spinel, mullite,  $\alpha$ - cristobalite, and depending upon the composition, the ternary compounds cordierite and sapphirine.

- iii) Presintering at 2700° and 2800°F results in formation of spinel and mullite to a greater extent than the 2600°F fire. The increasing temperature was found to increase the amount of these phases present.
- iv) Increases in the presintering temperature cause the reactions to proceed in the direction of equilibrium conditions. Under the influence of increased temperatures, only the compositions along the  $Al_2O_3$ -MgO binary reach completeness of reaction. All other compositions investigated proceeded in the direction of equilibrium conditions.
- v) Ternary compositions are formed during the 2600°F presinter, which with an increase in presintering temperature, melt incongruently to produce a slight liquid formation which enhances equilibrium phase reactions.
- vi) The phase reactions necessary to form spinel are occurring at the lowest presintering fire, and approach completeness of reaction about 2700°F.
- Vii) The phase reactions necessary to form mullite do not occur to any appreciable extent until 2700°F in the presintering fire.

b. Final Fire

- i) With a final firing of 2600°F, all phase reactions arrested in the presintering operation continue to progress toward equilibrium conditions. Ternary phases are present, in the cases of the low temperature presintering where the phases were present in the raw material, or where they had not yet been formed.
- ii) With a final firing of 2700°F, the mullite present has begun to dissociate into alumina and a liquid. There is a slight decrease in the spinel content as magnesia goes into the liquid. The alumina peaks are increasing as the mullite and spinel dissociate.
- iii) With a final firing of 2800°F, the mullite peaks in compositions containing 1:1 and 1:2 silica to magnesia ratios have disappeared, while those in the compositions containing 2:1 silica to magnesia ratios have substantially decreased. In the series containing 1:1 and 2:1 silica to magnesia ratios, the spinel has decreased slightly and the alumina peaks have increased in size. In the series with a 1:2 silica to magnesia ratio, the spinel peaks are increasing, while the alumina and mullite peaks are decreasing.



## 6. Densification

- a. Compositions undergoing the presintering fire show only a slight increase in density. The density increases with an increase in temperature, and the X-ray patterns show no substantial changes indicating liquid formation, therefore the slight densification occurring is realized through diffusional processes. The diffusional processes were hindered by the large void content introduced by the burnout of the binder.
- b. Compositions undergoing the final firing after fabrication utilizing the presintering process densify with the aid of a liquid phase. The character of the densification curve and the X-ray patterns show that a liquid phase is being formed in the firing range necessary to mature a presintered composition. This liquid phase enables the compositions to mature at lower temperatures than if only diffusional processes were operative.

## 7. Equilibrium

- a. The raw materials utilized in the final firing operation contain at least four components. These many component systems give use to complex phase reactions and liquid formation not described by the phase diagram as they proceed toward an equilibrium assemblage.

(  
b. The results attained in this study are of such a nature that they appear to resemble equilibrium conditions. However, there is no conformity between the reaction temperatures and those described by the phase diagram,

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## II. SINTERING STUDIES

### A. Introduction

An investigation of the densification of pure aluminum oxide with and without small additions of magnesia in vacuum was completed, and was reported in the last quarterly report. It has been found that the maturing temperature of pure alumina and alumina with small additions of magnesia has been considerably reduced, to 2820°F, when these compositions were fired in vacuum. In addition theoretically dense bodies have been prepared at 1750°C utilizing the 1/4% MgO composition. An investigation of the densification of these same compositions when fired in dry hydrogen and dry helium will be made. The effects made by these atmospheres on the sintering of alumina will be compared to the results obtained in vacuum. An understanding of the manner in which firing atmospheres and additives affect the sintering of pure aluminum oxide will enable better control of the sintering process. This in turn will reduce the firing temperature of high alumina ceramics and maintain or even increase the refractoriness of these compositions.

### B. Theoretical Considerations and Methods of Approach

The compositions that will be investigated range from 98.00%  $Al_2O_3$ , and 2.00% MgO to pure Alumina. Three compositions will be investigated in order to determine their sintering characteristics. These compositions are respectively 100%  $Al_2O_3$ , 99.75%  $Al_2O_3$  - 0.25% MgO and 98%  $Al_2O_3$  - 2.00% MgO.

As seen from the vacuum firings of these compositions in the previous report there seems to be a different mechanism operative in the sintering of these three compositions. It was postulated that this difference could be attributed to the formation of a solid solution of magnesia in pure alumina for the 1/4% MgO composition and the formation of both a solid solution and a second phase, namely spinel, at least at 1750 °C, for the 2.00% MgO composition. X-ray determinations will be made on 6 compositions varying the alumina content from between 98 to 100%  $Al_2O_3$ . These determinations when made using back reflections should yield a very precise measure of the d spacing. Any change in d spacing as MgO is added to pure Alumina indicates the formation of a solid solution of magnesia in alumina. When no further change of d spacing occurs as additional magnesia is added to alumina this signifies that the additional magnesia is forming a separate phase. In this way a calculation of the number of vacancies introduced in alumina by adding magnesia can be calculated. The effect of a solid solution and that of a solid solution and a second phase can be compared to the overall activation energy for sintering and an evaluation of these types of additions can be made. The X-ray determinations will be made for all six compositions for soaking temperatures of 1550, 1650, 1700, and 1750 °C and a constant soaking time of five hours.

The relation between solid solution and formation of a second phase will be evaluated as a function of temperature.

The above determinations of solid solution and total activation energy will be made for vacuum, dry hydrogen and dry helium. In this way a semi quantitative measure of the effect firing atmosphere has on the sintering of alumina can be obtained.

This will afford a large degree of control of the sintering of aluminum oxide. In this way control of grain size, bulk density can be obtained for near 100%  $Al_2O_3$ , compositions that do not contain a glassy phase. In addition, the maturing temperature of these compositions can be considerably reduced and the matured body will have much more desirable engineering properties than other bodies maturing within this temperature region.

#### C. Compositions

The compositions to be used in this investigation are:

1. 100%  $Al_2O_3$  - 0.00% MgO
2. 99.75%  $Al_2O_3$  - 0.25% MgO
3. 98%  $Al_2O_3$  - 2.00% MgO

In addition to the above mentioned compositions three other compositions were prepared for X-ray studies. Density and microstructure of these additional compositions will be compared at the five hour soaking time to the three major compositions.

These compositions are as follows:

1. 99.5%  $Al_2O_3$  - 0.50% MgO
2. 99%  $Al_2O_3$  - 1.00% MgO
3. 98.5%  $Al_2O_3$  - 1.50% MgO

#### D. Fabrication

One hundred gram batches were prepared of the six compositions under investigation. Alumina (Linde "A") was weighed on an analytical balance and placed in a glass jar. Magnesium nitrate solution, in the proper proportion was added to the batch. Five hundred milliliters of distilled water was added to form a slurry. The glass jar was sealed and agitated for half an hour, and the slurry poured into a pan covered with aluminum foil. The residual slurry was removed from the glass jar by repeated washings with distilled water and added to the pan. Next, the slurry was dried and placed into a jar. The residual material sticking to the aluminum foil was carefully scrapped off and placed into the jar making sure that no agglomerations had occurred. The dried material was agitated in the glass jar for 30 minutes and then removed and placed in an alumina mortar and pestle where sufficient distilled water to prepare a powdered compact was added. The batch was remixed and ground. In order to avoid the sticking of the batch to the die, one piece of paper was placed on each punch face. Discs of the raw material were prepared in hydraulic press with a 5/8" die, pressed to 50,000 psi and then removed and stored in a desiccation.

#### E. Firing Schedule

The 0.00% MgO, 0.25% MgO, and 2.00% MgO compositions will be fired for 1, 3, 5, and 7 hour soaks at temperatures of 1550, 1650, 1700 and 1750°C. The 0.5% MgO, 1.00% MgO and 1.50% MgO

compositions will be fired for 5 hour soaks at the four above mentioned temperatures. Soaks at the four above mentioned compositions will be made in atmospheres of dry hydrogen and dry helium. The latter three compositions will be fired in vacuum, dry hydrogen and dry helium.

#### F. Work to Date

A sufficient number of discs of each of the six compositions under investigation were prepared according to the fabrication technique described above. Discs of the six compositions were fired in vacuum for five hour soaks at 1550, 1650, 1700, and 1750°C. These have not been evaluated to date.

#### G. Future Work

Specimens of the 0.00%, 0.25% and 2.00% MgO compositions will be fired for 1, 3, 5, and 7 hour soaking periods at temperatures of 1550, 1650, 1700, and 1750°C respectively in dry hydrogen and dry helium atmospheres. Those of the 0.50%, 1.00% and 1.50% MgO compositions will be fired to 1550°, 1650°, 1700°, and 1750°F respectively for a 5 hour soaking period in dry hydrogen and dry helium atmospheres. Bulk density and total porosity measurements will be made on all six compositions under investigations.

### III. DEVITRIFICATION STUDIES

#### A. Introduction

As the speed of presently used aircraft increases to the point where the temperature of the radome exceeds approximately 200°F, and where rain erosion becomes a factor, ceramic radomes must be utilized. In the development of ceramic radome materials the principal effort has been placed on attaining excellent refractoriness. This type applications, and for radome temperature of up to between 1500 and 1800°F, the more refractory type ceramics are not necessary and ceramics other than high alumina become important. However the quality of the ceramics must be high (approaching true density) in order to realize good radar transmission. This quality is realized at the present time only with a prereacted materials.

Another approach to prereacted materials is advocated for this type application. Since the use temperatures involved are low, less refractory compositions which attain maturity at much lower temperatures should be utilized. Ternary compounds such as cordierite  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  and spodumens  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$  can be utilized. They have melting temperatures of approximately 2630° and 2500°F respectively. In order to attain good mixing of the raw materials involved in this type compositions the whole compositions is melted and poured into water to retain the glassy or randomly oriented structure. This now results in mixing of the compositions on an atomic basis. The quenched glass is reduced to a controlled particle size distribution



and fabricated. During a second firing a crystalline phase or phases devitrify and the specimen fires to the highest bulk density stage. Values of bulk density of 99% true density have been realized.

The object of this phase of the effort is to study radome materials by the devitrification approach of the prereacted raw materials technique. Compositions will be designated to mature at approximately 2300°F.

#### B. Approach to the Problem

The crystalline phase cordierite,  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  was selected for the initial study in this area. This crystalline phase is characterized by a rather low coefficient of linear thermal expansion of  $2 \times 10^{-6}$   $"/"/^\circ\text{C}$  between room temperature and 700°C. Its melting temperature is approximately 2630°F. Figure I on page shows the compositional location of the four compositions selected and Table I on page gives all compositions.

#### C. Procedure

The compositions were weighed and mixed for one hour in a V-blender. The raw material was placed in a fire clay crucible and placed in a pot furnace. The raw material was melted by heating to 2700°F, then quenched by pouring into cold water. The fritted material was ground in an alumina mill with alumina balls for 24 hours and passed through a 200 mesh screen.

Figure 1

COMPOSITIONS CHOSEN IN  
MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> PHASE DIAGRAM

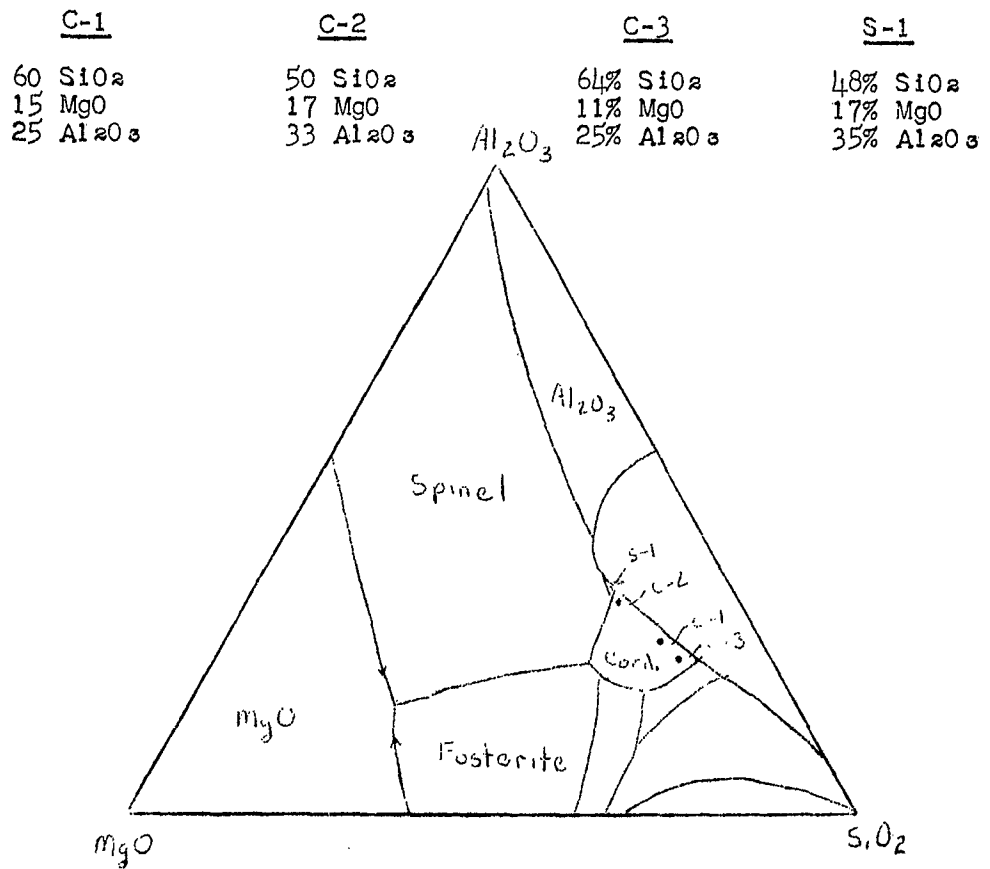


Figure 1

COMPOSITIONS AND RESULTS

<u>Compositions</u>	<u>C-1</u>	<u>C-2</u>	<u>C-3</u>	<u>S-1</u>
SiO <sub>2</sub> <sup>1</sup>	60%	50%	64%	48%
Al <sub>2</sub> O <sub>3</sub> <sup>2</sup>	25%	33%	25%	35%
MgO <sup>3</sup>	15%	17%	11%	17%

Moisture Absorption (5)

2100 °F	4.2	12.3	5.3	7.5
2250 °F	3.1	11.3	5.9	8.1
2350 °F	0.3	11.1	5.4	11.9
2450 °F	0.1	7.4	3.4	3.5

Bulk Density (g/cc)

2100 °F	2.24	1.90	2.23	2.13
2250 °F	2.23	1.93	2.19	2.09
2350 °F	2.36	1.95	2.18	2.04
2450 °F	2.45	2.08	2.22	2.25

Temperature of  
Initial Devitrification

1700 °F	1700 °F	1700 °F	1700 °F
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Crystalline Phases  
at 2450 °F

Cordierite	Cordierite	Cordierite	Cordierite
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1. A-14 Alumina, Alcoa
2. Supersil, Pennsylvania Glass Sand Corporation.
3. Magnesium Carbonate Mallenchrödt Chemical Works.

Specimens were prepared from all compositions by dry pressing in a steel die. In order to determine the devitrification and maturing temperatures these discs were fired in a gas furnace and one specimen of each composition was removed at 1100°, 1300°, 1500°, 1700°, 1900°, 2100°, 2250°, 2350°, and 2450°F respectively. The discs were analyzed by X-ray analysis for crystalline phases present, and density and moisture absorption determined.

#### D. Results

All results are presented in Table 1 on page . Composition C-1 was the only composition which approached maturity in the temperature range established. Its moisture absorption is 0.1% and bulk density is 2.45 g/cc. All other compositions do not contain sufficient glass to make them impervious. All compositions remain a glass up to 1700°F at which temperature crystallization or devitrification begins. Cordierite and alumina are present in all compositions. However, almost immediately alumina reacts to form more cordierite. Cordierite is the only crystalline phase present above 1700°F.

When crystallization takes place the compositions are quite porous and as the moisture absorption and bulk density data indicates, shrinkage takes place as the temperature is increased.

As noted above only composition C-1 matured at the maximum temperatures. Higher temperatures would mature the other three compositions. However, the object is to attain maturity at approximately 2300°F.

E. Future Work

The  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  system in the cordierite crystallization area will be further studied. Compositions will be selected and evaluated for physical and electrical properties. To control the properties and the maturing temperature additions effecting the glassy phase will be studied.